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NOVEL BLOCK COPOLYMERS AND METHOD FOR MAKING SAME

FIELD OF THE INVENTION

[0001] This invention relates to novel anionic block copolymers of mono alkenyl arenes and conjugated dienes, and to the methods for making such block copolymers. In particular, the invention relates to anionic block copolymers where one of the blocks is a controlled distribution copolymer of a conjugated diene and mono alkenyl arene having a specific structure of the monomers in the copolymer block.

BACKGROUND OF THE INVENTION

[0002] The preparation of block copolymers is well known. In a representative synthetic method, an initiator compound is used to start the polymerization of one monomer. The reaction is allowed to proceed until all of the monomer is consumed, resulting in a living homopolymer. To this living homopolymer is added a second monomer that is chemically different from the first. The living end of the first polymer serves as the site for continued polymerization, thereby incorporating the second monomer as a distinct block into the linear polymer. The block copolymer so grown is living until terminated.

[0003] Termination converts the living end of the block copolymer into a non-propagating species, thereby rendering the polymer non-reactive toward monomer or coupling agent. A polymer so terminated is commonly referred to as a diblock copolymer. If the polymer is not terminated the living block copolymers can be reacted with additional monomer to form a sequential linear block copolymer. Alternatively the living block copolymer can be contacted with multifunctional condensing agents commonly referred to as coupling agents. Coupling two of the living ends together results in a linear triblock copolymer having twice the molecular weight of the starting, living, diblock copolymer. Coupling more than two of the living diblock copolymer regions results in a radial block copolymer architecture having at least three arms.

[0004] One of the first patents on linear ABA block copolymers made with styrene and butadiene is U.S. Pat. 3,149,182. These polymers in turn could be hydrogenated

to form more stable block copolymers, such as those described in U.S. Pat. Nos.: 3,595,942 and Re. 27,145. In some cases what was desired was a random copolymer, such as an SBR, rather than a block copolymer. Random styrene butadiene copolymers or SBR are disclosed in U.S. Pat. Nos.: 2,975,160, 4,547,560, 4,367,325 and 5,336,737.

[0005] Inventors desiring a low melt viscosity in block copolymers considered the use of random styrene and butadiene blocks, as disclosed in U.S. Pat. 3,700,633. One means of introducing transparency to block copolymers was to also provide for random blocks, such as in U.S. Pat. Nos.: 4,089,913, 4,122,134 and 4,267,284.

[0006] When preparing random blocks of styrene and butadiene, so-called "tapered" blocks would result due to the fact that butadiene polymerizes at a faster rate than does styrene. See, e.g. U.S. Pat. Nos.: 5,191,024, 5,306,779 and 5,346,964. So in U.S. Pat. 4,603,155 The patentee prepared a block comprising multiple tapered blocks to achieve a more random copolymer. But in many cases the patentee relies on the continuous addition of both monomers and/or the use of randomizing agents to achieve a more random structure. Such techniques are disclosed in U.S. Pat. Nos. 3,700,633 and 4,412,087 and German patent applications DE 4420952, DE 19615533, DE 19621688, DE 195003944, DE 19523585, and DE 19638254. However, some randomizing agents will poison hydrogenation catalysts, and make the subsequent hydrogenation of the polymers difficult or impossible, so such randomizing agents must be avoided. Randomization agents containing N atoms are particularly prone to this problem.

[0007] In some cases it may be desired to achieve an even greater degree of structure in the polymer block, i.e. reduce or eliminate any excessive blockiness in the polymer. Thus, what is needed in the art is a method of effectively, and uniformly, copolymerizing various monomers wherein undesirable blockiness is avoided and undesirable effects occurring during post-polymerization hydrogenation treatments are also reduced or avoided.

SUMMARY OF THE INVENTION

[0008] Accordingly, in one aspect, the present invention relates to an unhydrogenated block copolymer having the general configuration A-B, A-B-A, or (A-B) n X, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein:

- a. each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene;
- b. each A block having an average molecular weight between about 3,000 and about 60,000 and each B block having an average molecular weight between about 30,000 and about 300,000;
- c. each B block comprises terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units;
- d. the total amount of mono alkenyl arene in the block copolymer is about 20 percent weight to about 80 percent weight; and
- e. the weight ratio of conjugated diene to mono alkenyl arene in the B block is between about 5:1 and about 1:2.

[0009] In another aspect, the present invention relates to a hydrogenated block copolymer having the general configuration A-B, A-B-A, or (A-B) n X, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein:

- a. prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene;
- b. subsequent to hydrogenation about 0-10 % of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced;
- c. each A block having an average molecular weight between about 3,000 and about 60,000 and each B block having an average molecular weight between about 30,000 and about 300,000;

- d. each B block comprises terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units;
- e. the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and
- f. the weight ratio of conjugated diene to mono alkenyl arene in the B block is between about 5:1 and about 1:2.

[0010] Still further, the present invention relates to processes for making such polymers. One of the processes comprises:

- a. polymerizing a mono alkenyl arene in a first reactor in the presence of an inert hydrocarbon solvent and an organolithium initiator whereby a living homopolymer block A1 terminated with a lithium ion is formed;
- b. adding to a second reactor an inert hydrocarbon solvent, 80 to 100% of the mono alkenyl arene monomer desired in the copolymer block B1, between 30 and 60% of the conjugated diene monomer desired in the copolymer block B1, and a randomization agent;
- c. transferring the living homopolymer block A1 to the second reactor and starting the polymerization of the mono alkenyl arene monomer and conjugated diene monomer added in step b; and
- d. after about 20 to about 60 mol percent of the monomers of step c have been polymerized, gradually adding the remaining amount of conjugated diene monomer and mono alkenyl arene to the second reactor at a rate that maintains the concentration of the conjugated diene monomer at not less than about 0.1% weight until about 90% of the monomers in block B1 have been polymerized, and the percentage of the mono alkenyl arene monomer in the unreacted monomer pool has been reduced to less than 20 % weight, thereby forming a living block copolymer A1B1.

[0011] Another process of the present invention involves:

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- a. polymerizing a mono alkenyl arene in a reactor in the presence of an inert hydrocarbon solvent and an organolithium Initiator whereby a living homopolymer block A1 terminated with a lithium ion is formed;
 - b. prior to the completion of the polymerization in step a, adding to the reactor in one aliquot between 40 and 60% of the conjugated diene monomer desired in the copolymer block B1, and a randomization agent and continuing the polymerization of the mono alkenyl arene monomer and conjugated diene monomer;
 - c. after about 20 to about 60 mole % of the monomers of step b have been polymerized, gradually adding the remaining amount of conjugated diene monomer and mono alkenyl arene to the second reactor at a rate that maintains the concentration of the conjugated diene monomer at no less than about 0.1% weight until about 90% of the monomers in block B1 have been polymerized and the percentage of the mono alkenyl arene monomer in the non-reacted monomer pool has been reduced to less than 20% weight, thereby forming a living copolymer block copolymer A1B1 ; and
 - d. adding additional mono alkenyl arene monomer to the reactor, thereby forming a living copolymer A1B1A2, wherein the A1 block and the A2 block each has an average molecular weight of about 3,000 to about 60,000 and the B1 block has an average molecular weight of about 30,000 to about 300,000.

[0012] In an alternative embodiment, the alkenyl arene monomer in block A1 is polymerized to completion, and monovinyl arene monomer and conjugated diene monomer are charged simultaneously, but the monovinyl arene monomer is charged at a much faster rate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figures 1, 2 and 3 shows the distribution of styrene and butadiene in the midblock of three separate S-S/B-S block copolymers. As shown in the Figures, the controlled distribution copolymer block of the present invention is characterized by the

presence of butadiene rich regions on the ends of the block and styrene rich regions near the middle or center of the controlled distribution block. Figure 4 is a plot of the tensile properties of block copolymers of the present invention containing styrene in the midblocks and having controlled distribution compared to normal and high vinyl polymers. All of the polymers in Figure 4 had nominal block molecular weights of 10,000-80,000-10,000.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention offers novel compositions and methods of preparing such in copolymerizing alkenyl arenes and dienes as part of a mono alkenyl arene/conjugated diene block copolymer. Surprisingly, the combination of (1) a unique order for the monomer addition and (2) the use of diethyl ether or other ethers as a component of the solvent (which will be referred to as "randomizing agents", in keeping with the common usage of the term) results in a certain marked uniformity of the distribution of the two monomers (herein termed a "controlled distribution" polymerization, i.e., a polymerization resulting in a "controlled distribution" structure), and also results in the presence of certain mono alkenyl arene rich regions and certain conjugated diene rich regions in the polymer block. For purposes hereof, "controlled distribution" is defined as referring to a molecular structure lacking well-defined blocks of either monomer, with "runs" of any given single monomer attaining a preferred maximum number average of about 20 units, as shown by either the presence of only a single T_g, intermediate between the T_g's of either monomer alone, when analyzed using differential scanning calorimetry ("DSC") (thermal) methods or via mechanical methods, or as shown via proton nuclear magnetic resonance ("H-NMR") methods. This controlled distribution structure is very important in managing the strength and T_g of the resulting copolymer, because the controlled distribution structure ensures that there is virtually no phase separation of the two monomers, i.e., in contrast with block copolymers in which the monomers actually remain as separate "microphases", with distinct T_g's, but are actually chemically bonded together. This controlled distribution structure assures that only one T_g is present and that, therefore, the thermal

performance of the resulting copolymer is predictable and, in fact, predeterminable. Furthermore, when a copolymer having such a controlled distribution structure is then used as one block in a di-block, tri-block or multi-block copolymer, the relatively higher Tg made possible by means of the presence of an appropriately-constituted controlled distribution copolymer region will tend to raise the heat resistance of the block copolymer as a whole. Modification of certain other properties is also achievable.

[0015] It is also an important aspect of the present invention that the subject copolymer block also has three distinct regions – conjugated diene rich regions on the end of the block and a mono alkenyl arene rich region near the middle or center of the block. What is desired is a mono alkenyl arene/conjugated diene controlled distribution copolymer block, wherein the proportion of mono alkenyl arene units increases gradually to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized.

[0016] Anionic, solution copolymerization to form the controlled distribution copolymers of the present invention can be carried out using, to a great extent, known and previously employed methods and materials. In general, the copolymerization is attained anionically, using known selections of adjunct materials, including polymerization initiators, solvents, promoters, and structure modifiers, but as a key feature of the present invention, in the presence of a randomization agent. Such randomization agent is, in preferred embodiments, a non-chelating ether. Examples of such ether compounds are cyclic ethers such as tetrahydrofuran and tetrahydropyran and aliphatic monoethers such as diethyl ether and dibutyl ether. In some cases, particularly where the vinyl content of the conjugated diene is to be over 50%, it may be necessary to use a chelating agent, including aliphatic polyethers such as diethylene glycol dimethyl ether and diethylene glycol diethyl ether. Preferably the ether is an aliphatic monoether, and more preferably diethyl ether. Such copolymerization can be conducted as a batch, semi-batch, or continuous preparation, with batch being most preferred, but regardless, it is important that the randomization agent be present in the selected solvent prior to or concurrent with the beginning of the polymerization process.

[0017] Without wishing to be bound by any theory, it is theorized that the randomization agent increases the polarity of the bulk solvent mixture, i.e., it serves as a "bulk modifier". Typically, polar compounds have not been selected for incorporation into the polymerization solution simply because they are not essential to promote the formation of terminal polymer blocks when typical initiators are used. Consequently, introduction of the polarity-increasing compound, i.e., the randomization agent, counteracts the preference of the initiator to attach to one monomer over another. For example, in the case of styrene and a diene, the preference would be toward the diene. This polarity increase then operates to promote more efficient "controlled distribution" copolymerization of the two monomers because the living chain end "sees" one monomer approximately as easily as it "sees" the other. The polymerization process is thereby "tuned" to allow incorporation of each of the monomers into the polymer at nearly the same rate. Such a process results in a copolymer having no "long runs" of either of the monomer components – in other words, a controlled distribution copolymer as defined hereinabove. More specifically, in the presence of these modifiers the rate of addition of the monovinyl arene monomer to a growing chain end derived from the conjugated diene monomer is only moderately slower than the addition of another molecule of the conjugated diene monomer. However, the rate of addition of a molecule of the conjugated diene monomer to a growing chain end derived from the monovinyl arene is much faster than the rate of adding a second molecule of the monovinyl arene monomer. Since the conjugated diene still polymerizes faster, the portion of the B region that is formed at the start of the polymerization will be rich in the conjugated diene. As the polymerization proceeds, the monomer pool becomes richer in the monovinyl arene, driving more of this monomer into the growing chain. In the preferred process, the monovinyl arene monomer will be nearly consumed by the time that the slow addition of the second aliquot is complete, so that the polymerization ends rich in the conjugated diene. Short blocks of the conjugated diene monomer may be formed throughout the polymerization, but blocks of the monovinyl arene monomer are only formed when the concentration of the conjugated diene monomer becomes quite low. Under the preferred conditions, the cumulative percentage of the monovinyl arene

monomer in the B block peaks at about 40% - 60% overall conversion, but only exceeds the final value by about 25% - 30%. The result of this relatively uniform distribution of monomers is a product having a single Tg, which is a weighted average of the Tg values of the two corresponding homopolymers.

[0018] As noted above, the randomization agent is preferably a non-chelating ether. By "non-chelating" is meant that such ethers will not chelate with the growing polymer, that is to say, they will not form a specific interaction with the chain end, which is derived from the initiator compound (e.g., lithium ion). Because the non-chelating ethers used in the present invention operate by modifying the polarity of the entire polymerization charge, they are preferably used in relatively large concentrations. Where diethyl ether, which is preferred, is selected, it is preferably at a concentration from about 1 to about 10 percent, by weight of the polymerization charge (solvent and monomers), and more preferably from about 3 to about 6 percent by weight. Higher concentrations of this monoether can alternatively be used, but appear to increase cost without added efficacy.

[0019] An important aspect of the present invention is to control the microstructure or vinyl content of the conjugated diene in the controlled distribution copolymer block. The term "vinyl content" refers to the fact that a conjugated diene is polymerized via 1,2-addition (in the case of butadiene – it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3-butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain. When referring to the use of butadiene as the conjugated diene, it is preferred that about 20 to about 80 mol percent of the condensed butadiene units in the copolymer block have 1,2 vinyl configuration. Preferably about 30 to about 70 mol percent of the condensed butadiene units should have 1,2 configuration. This is effectively controlled by varying the relative amount of the randomization agent. As will be appreciated, the randomization agent serves two purposes – it creates the controlled distribution of the mono alkenyl arene and conjugated diene, and also controls the

microstructure of the conjugated diene. Suitable ratios of randomization agent to lithium are disclosed and taught in US Pat. Re 27,145, which disclosure is incorporated by reference.

[0020] The solvent used as the polymerization vehicle may be any hydrocarbon that does not react with the living anionic chain end of the forming polymer, is easily handled in commercial polymerization units, and offers the appropriate solubility characteristics for the product polymer. For example, non-polar aliphatic hydrocarbons, which are generally lacking in ionizable hydrogens make particularly suitable solvents. Frequently used are cyclic alkanes, such as cyclopentane, cyclohexane, cycloheptane, and cyclooctane, all of which are relatively non-polar. Other suitable solvents will be known to the skilled routineer and can be selected to perform effectively in a given set of process conditions, with temperature being one of the major factors taken into consideration.

[0021] Starting materials for preparing the novel controlled distribution copolymers of the present invention include the initial monomers. The alkenyl arene can be selected from styrene, alpha-methylstyrene, para-methylstyrene, vinylnaphthalene, and para-butyl styrene. Of these, styrene is most preferred and is commercially available, and relatively inexpensive, from a variety of manufacturers. The conjugated dienes for use herein are 1,3-butadiene and substituted butadienes such as isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, and 1-phenyl-1,3-butadiene, or mixtures thereof. Of these, 1,3-butadiene is most preferred.

[0022] Other important starting materials for anionic copolymerizations include one or more polymerization initiators. In the present invention such include, for example, alkyl lithium compounds and other organolithium compounds such as s-butyllithium, n-butyllithium, t-butyllithium, amyllithium and the like. Of these, s-butyllithium is preferred. The initiator can be used in the polymerization mixture (including monomers and solvent) in an amount calculated on the basis of one initiator molecule per desired polymer chain. The lithium initiator process is well known and is described in, for

example, U.S. Patents 4,039,593 and Re. 27,145, which descriptions are incorporated herein by reference.

[0023] Polymerization conditions to prepare the novel copolymers of the present invention are typically similar to those used for anionic polymerizations in general. In the present invention polymerization is preferably carried out at a temperature of from about -30° to about 150°C , more preferably about 10° to about 100°C , and most preferably, in view of industrial limitations, about 30° to about 90°C . It is carried out in an inert atmosphere preferably nitrogen, and may also be accomplished under pressure within the range of from about 0.5 to about 10 bars. This copolymerization generally requires less than about 12 hours, and can be accomplished in from about 5 minutes to about 5 hours, depending upon the temperature, the concentration of the monomer components, the molecular weight of the polymer and the amount of randomization agent that is employed.

[0024] As discussed above, an important discovery of the present invention is the control of the monomer feed during the polymerization of the controlled distribution block. According to the present invention about 80 to 100 percent of the monoalkenyl arene is added to the reactor, along with about 30 to about 60 percent of the conjugated diene. The monomers are then caused to start polymerization. After about 20 to 60 mol percent of the monomers have polymerized, the remaining portion of the mono alkenyl arene (if any) is added and the remaining conjugated diene monomer is gradually added at a rate that maintains the concentration of the conjugated diene monomer at no less than about 0.1% weight until about 90% of the monomers in block B1 have been polymerized, and the percentage of the monoalkenyl arene monomer in the non-reacted monomer pool has been reduced to less than 20% weight, preferably less than 15% weight. In this way the formation of styrene blocks is prevented throughout the majority of the polymerization and there is sufficient conjugated diene at the end of the polymerization to prevent excessive blockiness of the mono alkenyl arene. The resulting polymer block has diene rich regions near the beginning and the end of the block and an arene rich region near the center of the block. Typically the first 15 to 25% and the last 75 to 85% of the block are diene rich, with the remainder

considered to be arene rich. The term "diene rich" means that the region has a measurably higher ratio of diene to arene than the center region. Another way to express this is the proportion of mono alkenyl arene units increases gradually along the polymer chain to a maximum near the middle or center of the block and then decreases gradually until the polymer block is fully polymerized. In a preferred embodiment, all of the mono alkenyl arene and about 30 percent of the conjugated diene are charged to the reactor, and the remainder of the conjugated diene is added after about 30 to about 50 percent of the original monomers have polymerized.

[0025] For the controlled distribution block the weight ratio of conjugated diene to mono alkenyl arene is between about 5:1 and about 1:2, preferably between about 3:1 and about 1:1.

[0026] A particular feature of the present invention is that the resultant copolymer is relatively uniform in its distribution of the two monomers within a polymer chain, thus offering the improvements in Tg and property modification suggested by the identity of the starting monomers. A proton (hydrogen) nuclear magnetic resonance (H-NMR) procedure may preferably be used to assay for this advantageous controlled distribution, using techniques known to those skilled in the art. Alternatively, a differential scanning calorimetry (DSC) method may be used as an assay, determining the controlled structure of the polymerization by confirming the presence of a desired single Tg as is characteristic of a controlled distribution copolymer.

[0027] The potential for blockiness can also be inferred from measurement of the UV-visible absorbance in a wavelength range suitable for the detection of polystyryllithium end groups during the polymerization of the B block. A sharp and substantial increase in this value is indicative of a substantial increase in polystyryllithium chain ends. In this process, this will only occur if the conjugated diene concentration drops below the critical level to maintain controlled distribution polymerization. Any styrene monomer that is present at this point will add in a blocky fashion. The term "styrene blockiness" is defined to be the proportion of S units in the polymer having two S nearest neighbors on the polymer chain. Expressed thus,

Polymer-Bd-S-(S)_n-S-Bd-Polymer, where n greater than zero is defined to be blocky styrene. For example, if n equals 8 in the example above, then the blockiness index would be 80%.

[0028] As used herein, "thermoplastic block copolymer" is defined as a block copolymer having at least a first block of a mono alkenyl arene, such as styrene and a second block of a controlled distribution copolymer of diene and mono alkenyl arene. The method to prepare this thermoplastic block copolymer is via any of the methods generally known for block polymerizations. The present invention includes as an embodiment a thermoplastic copolymer composition, which may be either a di-block, tri-block copolymer or multi-block composition. In the case of the di-block copolymer composition, one block is the alkenyl arene-based homopolymer block and polymerized therewith is a second block of a controlled distribution copolymer of diene and alkenyl arene. In the case of the tri-block composition, it comprises, as end-blocks the glassy alkenyl arene-based homopolymer and as a mid-block the controlled distribution copolymer of diene and alkenyl arene. Where a tri-block copolymer composition is prepared, the controlled distribution diene/alkenyl arene copolymer can be herein designated as "B" and the alkenyl arene-based homopolymer designated as "A". The A-B-A, tri-block compositions can be made by either sequential polymerization or coupling. In the sequential solution polymerization technique, the mono alkenyl arene is first introduced to produce the relatively hard aromatic block, followed by introduction of the controlled distribution diene/alkenyl arene mixture to form the mid block, and then followed by introduction of the mono alkenyl arene to form the terminal block. In addition to the linear, A-B-A configuration, the blocks can be structured to form a radial (branched) polymer, (A-B)_nX, or both types of structures can be combined in a mixture. Some A-B diblock polymer can be present but preferably at least about 70 weight percent of the block copolymer is A-B-A or radial (or otherwise branched so as to have 2 or more terminal resinous blocks per molecule) so as to impart strength.

[0029] Preparation of radial (branched) polymers requires a post-polymerization step called "coupling". In the above radial formula n is an integer of from 2 to about 30, preferably from about 2 to about 15, and X is the remnant or residue of a coupling

agent. A variety of coupling agents are known in the art and include, for example, dihalo alkanes, silicon halides, siloxanes or esters of monhydric alcohols with carboxylic acids, and epoxidized oils. Star-shaped polymers are prepared with polyalkenyl coupling agents as disclosed in, for example, U.S. Patents Numbers 3,985,830; 4,391,949; and 4,444,953; Canadian Patent Number 716,645. Suitable polyalkenyl coupling agents include divinylbenzene, and preferably m-divinylbenzene.

[0030] Additional possible post-polymerization treatments that can be used to further modify the configuration of the polymers and therefore their properties include capping and chain-termination. Capping agents, such as ethylene oxide, carbon dioxide, or mixtures thereof serve to add functional groups to the chain ends, where they can then serve as reaction sites for further property-modifying materials. In contrast, chain termination simply prevents further polymerization and thus prevents molecular weight growth beyond a desired point. This is accomplished via the deactivation of active metal atoms, particularly active alkali metal atoms, and more preferably the active lithium atoms remaining when all of the monomer has been polymerized. Effective chain termination agents include water; alcohols such as methanol, ethanol, isopropanol, 2-ethylhexanol, mixtures thereof and the like; and carboxylic acids such as formic acid, acetic acid, maleic acid, mixtures thereof and the like. See, for example, U.S. Patent 4,788,361, the disclosure of which is incorporated herein by reference. Other compounds are known in the prior art to deactivate the active or living metal atom sites, and any of these known compounds may also be used. Alternatively, the living copolymer may simply be hydrogenated to deactivate the metal sites.

[0031] The polymerization procedures described hereinabove, including preparation of the diene/alkenyl arene copolymer and of di-block and multi-block copolymers prepared therewith, can be carried out over a range of solids content, preferably from about 5 to about 80 percent by weight of the solvent and monomers, most preferably from about 10 to about 40 weight percent. For high solids polymerizations, it is preferable to add any given monomer, which may include, as previously noted, a previously prepared homopolymer or copolymer, in increments to avoid exceeding the desired polymerization temperature. Properties of a final tri-block polymer are

dependent to a significant extent upon the resulting alkenyl content and diene content. It is preferred that, to ensure significantly elastomeric performance while maintaining desirably high Tg and strength properties, as well as desirable transparency, the tri-block and multi-block polymer's alkenyl arene content is greater than about 20 % weight, preferably from about 20% to about 80 % weight. This means that essentially all of the remaining content, which is part of the diene/alkenyl arene block, is diene.

[0032] It is also important to control the molecular weight of the various blocks. For an AB diblock, desired block weights are 3,000 to about 60,000 for the mono alkenyl arene A block, and 30,000 to about 300,000 for the controlled distribution conjugated diene/mono alkenyl arene B block. Preferred ranges are 5000 to 45,000 for the A block and 50,000 to about 250,000 for the B block. For the triblock, which may be a sequential ABA or coupled (AB)₂X block copolymer, the A blocks should be 3,000 to about 60,000, preferably 5000 to about 45,000, while the B block for the sequential block should be about 30,000 to about 300,000, and the B blocks (two) for the coupled polymer half that amount. The total average molecular weight for the triblock copolymer should be from about 40,000 to about 400,000, and for the radial copolymer from about 60,000 to about 600,000. These molecular weights are most accurately determined by light scattering measurements.

[0033] An important feature of the thermoplastic elastomeric di-block and tri-block polymers of the present invention, including one or more controlled distribution diene/alkenyl arene copolymer blocks and one or more mono alkenyl arene blocks, is that they have at least two Tg's, the lower being the combined Tg of the controlled distribution copolymer block which is an intermediate of its constituent monomers' Tg's. Such Tg is preferably at least about -60 degrees C, more preferably from about - 40 degrees C to about zero degrees C, and most preferably from about - 40 degrees C to about - 10 degrees C. The second Tg, that of the mono alkenyl arene "glassy" block, is preferably from about 80 degrees C to about 110 degrees C, more preferably from about 80 degrees C to about 105 degrees C. The presence of the two Tg's, illustrative of the microphase separation of the blocks, contributes to the notable elasticity and

strength of the material in a wide variety of applications, and its ease of processing and desirable melt-flow characteristics.

[0034] It should be noted that, in yet another embodiment of the present invention, additional property improvements of the compositions hereof can be achieved by means of yet another post-polymerization treatment, that of selective hydrogenation of the diene portions of the final block copolymer. Hydrogenation generally improves thermal stability, ultraviolet light stability, oxidative stability, and, therefore, weatherability of the final polymer. A major advantage of the present invention is that the randomization agent, such as the non-chelating monoether, which is present during the initial polymerization process, does not interfere with or otherwise "poison" the hydrogenation catalyst, and thus the need for any additional removal steps is obviated.

[0035] Hydrogenation can be carried out via any of the several hydrogenation or selective hydrogenation processes known in the prior art. For example, such hydrogenation has been accomplished using methods such as those taught in, for example, U.S. Patents 3,494,942; 3,634,594; 3,670,054; 3,700,633; and Re. 27,145, the disclosures of which are incorporated herein by reference. These methods operate to hydrogenate polymers containing aromatic or ethylenic unsaturation and are based upon operation of a suitable catalyst. Such catalyst, or catalyst precursor, preferably comprises a Group VIII metal such as nickel or cobalt which is combined with a suitable reducing agent such as an aluminum alkyl or hydride of a metal selected from Groups I-A, II-A and III-B of the Periodic Table of the Elements, particularly lithium, magnesium or aluminum. This preparation can be accomplished in a suitable solvent or diluent at a temperature from about 20°C to about 60°C. Other catalysts that are useful include titanium based catalyst systems.

[0036] Hydrogenation can be carried out under such conditions that at least about 90 percent of the conjugated diene double bonds have been reduced, and between zero and 10 percent of the arene double bonds have been reduced. Preferred ranges are at least about 95 percent of the conjugated diene double bonds reduced, and more preferably about 98 percent of the conjugated diene double bonds are reduced.

Alternatively, it is possible to hydrogenate the polymer such that aromatic unsaturation is also reduced beyond the 10 percent level mentioned above. In that case, the double bonds of both the conjugated diene and arene may be reduced by 90 percent or more.

[0037] Once the hydrogenation is complete, it is preferable to extract the nickel catalyst by stirring with the polymer solution a relatively large amount of aqueous acid (preferably 20-30 percent by weight), at a volume ratio of about 0.5 parts aqueous acid to 1 part polymer solution. Suitable acids include phosphoric acid, sulfuric acid and organic acids. This stirring is continued at about 50°C for about 30 to about 60 minutes while sparging with a mixture of oxygen in nitrogen.

[0038] In an alternative, the block copolymer of the present invention may be functionalized in a number of ways. One way is by treatment with an unsaturated monomer having one or more functional groups or their derivatives, such as carboxylic acid groups and their salts, anhydrides, esters, imide groups, amide groups, and acid chlorides. The preferred monomers to be grafted onto the block copolymers are maleic anhydride, maleic acid, fumaric acid, and their derivatives. A further description of functionalizing such block copolymers can be found in Gergen et al, U.S. Pat. No. 4,578,429 and in U. S. Pat. No. 5,506,299. In another manner, the selectively hydrogenated block copolymer of the present invention may be functionalized by grafting silicon or boron containing compounds to the polymer as taught in U.S. Pat. No. 4,882,384. In still another manner, the block copolymer of the present invention may be contacted with an alkoxy-silane compound to form silane-modified block copolymer. In yet another manner, the block copolymer of the present invention may be functionalized by grafting at least one ethylene oxide molecule to the polymer as taught in U.S. Pat. No. 4,898,914, or by reacting the polymer with carbon dioxide as taught in U. S. pat. No. 4,970,265. Still further, the block copolymers of the present invention may be metallated as taught in U.S. Pat. Nos. 5,206,300 and 5,276,101, wherein the polymer is contacted with an alkali metal alkyl, such as a lithium alkyl. And still further, the block copolymers of the present invention may be functionalized by grafting sulfonic groups to the polymer as taught in U. S. 5,516,831. All of the patents mentioned in this paragraph are incorporated by reference into this application.

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[0039] The last step, following all polymerization(s) as well as any desired post-treatment processes, is a finishing treatment to remove the final polymer from the solvent. Various means and methods are known to the skilled routineer, and include use of steam to evaporate the solvent, and coagulation of the polymer followed by filtration. The final result is a "clean" block copolymer useful for a wide variety of challenging applications, according to the properties thereof. These properties include, for example, the final polymer's stress-strain response, which shows that a composition of the present invention exhibits a stiffer rubbery response to strain, therefore requiring more stress to extend the same length. This is an extremely useful property that allows the use of less material to achieve the same force in a given product. Elastic properties are also modified, exhibiting increasing modulus with increasing elongation, and there is a reduced occurrence of the rubbery plateau region where large increases in elongation are required to procure an increase in stress. Another surprising property is increased tear strength. The controlled distribution copolymers of the present invention offer additional advantage in their ability to be easily processed using equipment generally designed for processing thermoplastic polystyrene, which is one of the most widely known and used alkenyl arene. Melt processing can be accomplished via extrusion or injection molding, using either single screw or twin screw techniques that are common to the thermoplastics industry. Solution or spin casting techniques can also be used as appropriate.

[0040] The polymers of the present invention are useful in a wide variety of applications including, for example, molded and extruded goods such as toys, grips, handles, shoe soles, tubing, sporting goods, sealants, gaskets, and oil gels. The compositions also find use as rubber toughening agents for polyolefins, polyamides, polyesters and epoxy resins. Improved elasticity when compared with conventional styrenic block copolymers makes these copolymers particularly useful for adhesives, including both pressure-sensitive and hot-melt adhesives.

[0041] A particularly interesting application is thermoplastic films which retain the processability of styrenic block copolymers but exhibit a higher "elastic power" similar to spandex polyurethanes. As compounded with polyethylene or with a combination of

tackifying resin and polyethylene, the controlled distribution copolymers of the present invention can meet these performance expectations. The resultant films show significant improvements in puncture resistance and strength, and reduced viscosity, when compared with common styrene/ethylene-butylene block copolymers. The same controlled distribution styrene/butadiene (20/80 wt/wt) copolymer can also be formulated in a film compound with oil and polystyrene, wherein it exhibits higher strength and improved energy recovery and transparency in comparison with a control formulation based on a styrene/ethylene-butylene/styrene block copolymer. In molding applications formulated using oil and polypropylene, reduced viscosity and coefficients of friction also offer expansion in applications such as cap seals, which may be able to be produced without undesirable slip agents which may bloom and contaminate contents.

[0042] Finally, the copolymers of the present invention can be compounded with other components not adversely affecting the copolymer properties. Exemplary materials that could be used as additional components would include, without limitation, pigments, antioxidants, stabilizers, surfactants, waxes, flow promoters, solvents, particulates, and materials added to enhance processability and pellet handling of the composition.

[0043] The following examples are intended to be illustrative only, and are not intended to be, nor should they be construed as being, limitative in any way of the scope of the present invention.

ILLUSTRATIVE EMBODIEMENT #1

[0044] A general procedure was used to effectively randomize the anionic copolymerization of 1,3-butadiene (Bd) and styrene (S) in the presence of diethyl ether (DEE). A number of block copolymer mixtures of S-S/E/B-S triblocks were synthesized stepwise in cyclohexane. DEE was used to randomize the copolymerization of styrene and butadiene in the -S/E/B- rubber midblock. During the copolymerization step, a

number of samples were collected as the reaction progressed to enable H-NMR characterization of the degree of monomer randomization.

[0045] For Step I, an appropriate amount of polymerization grade cyclohexane was charged to a well-mixed 60-gallon stainless steel reactor vessel at 30°C. Pressure in the reactor vessel was controlled with nitrogen gas. Styrene monomer was charged to the reactor at 30°C. 10 ml increments of sec-butyllithium (12 wt.) were added to the reactor to titrate the cyclohexane and styrene monomer mixture. The titration endpoint was determined with an on-line colorimeter. After titration, a gig of excess sec-butyllithium was then added to the reactor to initiate the anionic polymerization of the living polystyrene blocks. The temperature was allowed to increase to 55°C and the reaction was carried out to 99.9% conversion of the styrene. This completed the first styrene block of this block copolymer, (S)-.

[0046] For Step II, an appropriate amount of polymerization grade cyclohexane was charged to a well-mixed 130-gallon stainless steel reactor vessel at 30°C. First, all of the styrene monomer required in the Step II reaction was charged to the reactor. Second, one-half of the butadiene monomer required in the Step II reaction was charged to the reactor. Third, an appropriate amount of diethyl ether was charged to the reactor. Fourth, 10 ml increments of sec-butyllithium (12 %wt.) were added to the reactor to titrate the cyclohexane, styrene monomer, butadiene monomer and diethyl ether mixture. The titration endpoint was determined with an on-line colorimeter. After titration, the living polystyrene chains were transferred via nitrogen pressure from the Step I reactor vessel to the Step II reactor vessel to initiate the Step II copolymerization reaction of styrene and butadiene at 30°C. Ten minutes after the initiation of the copolymerization, the remaining one-half of the butadiene monomer was dosed to the Step II reactor at a rate that kept the overall polymerization rate nearly constant. The temperature was allowed to increase to 55°C and the reaction was carried out to 99.9% conversion basis butadiene kinetics. This completed the addition of a styrene-butadiene randomized midblock to the Step I polystyrene block. The polymer structure at this point is (S)-(S/B)-.

[0047] For Step III, more styrene monomer was charged to the Step II reactor vessel at 55°C to react with the living (S)-(S/B)- polymer chains. The Step III reaction was maintained at near isothermal conditions until 99.9% conversion of the styrene. The living polymer chains were terminated by adding an appropriate amount of high-grade methanol to the final reactor solution. The final polymer structure was (S)-(S/B)-(S).

[0048] This type of experiment was executed 8 times over a range of varying styrene-butadiene midblock compositions. The analytical results from each of the 8 experiments are given in Table 1. The conditions for polymerization for each experiment are given in Table 2. Table 3 shows the polymer architecture for the various polymers. Regarding Table 3, the "Block Size" values were determined using GPC analyses taken on aliquots of polymer cement collected at the end of each step of the polymerization for each of the polymer preparations. These values reflect true molecular weights for each of the blocks. The values for "Blockiness of S in Step II Region (%)" were calculated from H-NMR data collected on aliquots of polymer cement taken at the end of the Step II polymerization for each of the experiments. The H-NMR analysis afforded a measure of the blockiness (percentage of styrene units in the polymer backbone present in multiplets of three or more) of styrene in the diblock copolymer formed at the end of Step II. This blockiness included the styrene blockiness of the Step I polystyrene region as well as the blockiness (if any) of the styrene in the controlled distribution styrene/butadiene copolymer prepared in Step II. To get the value of the blockiness of the styrene in the controlled distribution region of the copolymer, the blocky styrene content of the Step I region was subtracted from the total blockiness using a mathematical manipulation. This calculation gave the results reported for polymers 4 through 7. This analysis found few (1-7%), if any, styrene multiplets in the controlled distribution copolymer regions of these polymers. These data reflect the robust nature of the process described in the present invention. Polymers 1, 2 and 3 were not analyzed (NA) for styrene blockiness.

[0049] Figures 1, 2 and 3 depict the monomer distribution in the Bd/S block of 3 of the polymers prepared in this embodiment. The data in these figures was obtained by taking aliquots of the living polymerization solution at various times during the synthesis

of the Step II block of the S-S/Bd-S preparations, that is during the controlled distribution copolymerization of butadiene and styrene portion of the block copolymer preparation. The polybutadiene and polystyrene compositions of each of these aliquots was measured using an H-NMR technique. These "raw data" were adjusted by subtracting out the polystyrene component of the Step I polystyrene block from cumulative polystyrene content of the aliquot. The remainder gave the polystyrene component of the Step II block for each aliquot. The ratio of the polybutadiene content in moles to the polystyrene content in moles (as calculated in this way) was plotted against the level of conversion for each of the aliquots in each of the experiments. The molecular weight of each of the aliquots was measured using an H-NMR method, as well. The molecular weight of the Step II block for each of the aliquots was obtained by subtracting the molecular weight of the Step I block from the molecular weight of the aliquot. The molecular weight of the Step II block for the final aliquot was taken as the total molecular weight for this region (100% conversion). The level of conversion of each of the aliquots was calculated by taking the ratio of the Step II molecular weight for that aliquot to the molecular weight of the final Step II aliquot for that polymerization.

[0050] These plots clearly show the benefit of the present invention. The controlled distribution polymerization, in each case, starts out and ends with a relatively high ratio of incorporated butadiene to styrene (butadiene rich). Clearly there are no runs of polystyrene on either end of the Step II region, thus the control of end block molecular weight is determined only by the size the Step I and Step III styrene charges and the number of living chain ends in those polymerization Steps. The Step I and Step III polystyrene block sizes are not augmented by the addition of polystyrene runs at the start not at the end of the Step II polymerization.

[0051] It is significant to note that even though the center portion of the Step II regions in each of these polymerizations was richer in styrene (had a lower Bd/S ratio) there still were few, if any, styrene multiplets (<10 mol% of the styrene) incorporated into the polymer chain during this stage of the polymerization, as analyzed by H-NMR. A controlled distribution incorporation of the styrene monomer into the polymer chain was observed even though the relative rate of incorporation of styrene to butadiene had

increased during this part (from about 40% to about 60 % conversion of the Step II polymerization) of the polymerization. Such a controlled distribution incorporation of styrene in these copolymerization reactions seems to be necessary to obtain the desired stiffer stretch performance in the S-S/E/B-S product block copolymers.

ILLUSTRATIVE EMBODIMENT #II

[0052] In Illustrative Embodiment II various polymers of the present invention are compared against polymers of the prior art. All the polymers were linear ABA block copolymers made with styrene and butadiene monomers, and had nominal or target molecular weights of 10,000 for each of the A end blocks and 80,000 for the B mid block. Polymers 2 and 3 from Illustrative Embodiment I were used in this example. Polymers C-1 and C-2 are for comparison, and do not have any styrene in the B mid block. C-1 has a higher vinyl 1,2 content of 68%, while C-2 has a vinyl 1,2 content of 38%. Polymer C-3 was prepared with about 20 percent weight styrene in the B mid block. Polymer C-3 was prepared in a conventional polymerization process, wherein the mid block was prepared by co-polymerization of butadiene and styrene with a chelating randomization agent, but without controlled addition of the butadiene and styrene monomers. Rather, all the butadiene and styrene were added to the reactor at the start of the mid block polymerization along with the randomization agent (1,2 diethoxy propane). Accordingly, Polymer C-3 does not have a "controlled distribution" structure. Details on the block molecular weights and vinyl 1,2 contents are shown in Table 4.

[0053] Films were prepared from the polymers and tensile tested according to ASTM D412, and the results are shown in Table 5. The goal of the current invention is to make polymers that have a stiffer elastic response than Polymer C-2, a polymer that is well known in the art. Increasing the vinyl content without the controlled addition of styrene to block B, as shown in Polymer C-1, reduces the stiffness as shown in Figure 4. The 500% modulus in Table 5 demonstrates this response as well. The polymers of the present invention – Polymers 2 and 3 – exhibit stiffer elastic behavior as shown by

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Figure 4 and the 500% modulus in Table 5. The importance of controlling the distribution of styrene in the B mid block is illustrated by Polymer C-3. Although it is similar in composition to Polymer 3, its 500% modulus and general elastic properties are not improved over Polymer C-2, the standard of the current art.

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TABLE 1:

Polymer Step Number	Step MW(k)	IStep MW(k)	IIStep MW(k)	III%Styrene Step II	Styrene Blockiness	1,2-BD (%)	PSC (%)
1	10.5	106.3	118.6	12.6	65.6	34.5	29.75
2	10.5	98.6	110.8	12.5	65	38	29.53
3	9.2	90.6	99.9	24.9	50	35.8	40.12
4	9.7	92.3	102.8	37.6	43	35.3	48.3
5	13.9	140.8	158.2	37.6	43	35	50.15
6	10.6	101.4	112.6	25.1	49	36.2	40
7	10.3	99.3	111.9	25.2	51	37.1	40.31
8	8.2	91.2	98.9	25.1	43.9	37	37

In Table 1, "MW(k)" = molecular weight in thousands, "Styrene Blockiness" = the blockiness of all of the styrene units in the final polymer as measured using an H-NMR technique, "1,2-Bd(%)" = the vinyl content of the butadiene part of the polymer, and "PSC(%)" = weight percent of styrene in the final polymer.

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Table 2: Conditions for Polymerization of S/B Mid Block Copolymers

Polymer #		1	2	3	4	5	6	7	8
Step I									
Charge Cyclohexane	kg	40	40	40	40	59.8	60	60.4	40.8
Charge Styrene	kg	10.04	10	10.2	10.1	15.05	15.1	15.1	10.2
sBuLi Titration (12 wt%)	ml	20	20	20	55	10	5	20	10
Excess sBuLi (12 wt%)	ml	755	755	800	754	745	1065	1062	875
Start Temperature	Deg C	30	30	30	30	30	30	30	30
Final Temperature	Deg C	55	50	55	55	55	55	55	55
Step II									
Charge Cyclohexane	kg	170	165	165	200	198	283.4	281	202.7
Charge Styrene	kg	5.05	5	10.02	18.1	18.1	17.12	17.12	11.98
Charge Butadiene	kg	17.5	17.23	15.5	15.05	15.1	25.6	25.5	18
Charge Diethyl Ether	kg	15	15.1	15.1	18.3	18	25.7	25.6	18.2
sBuLi Titration (12 wt%)	ml	30	25	20	55	50	130	100	70
Transfer Step I Cement	kg	25.1	25.5	25.2	30.8	30.5	42.3	42.9	25.6
Step I Cement Transfer Rate	kg/min	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Start Butadiene Program @	min	10	10	10	10	10	10	10	10
Program Butadiene	kg	17.5	17.77	14.5	15.02	15	25.5	25.1	17.8
Butadiene Program Rate	kg/min	0.29	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Start Temperature	Deg C	30	30	30	30	30	30	30	30
Final Temperature	Deg C	55	55	55	55	55	55	55	55
Step III									
Program Styrene	kg	5	5	4.9	5.9	5.8	8.5	8.4	4.2
Styrene Program Rate	kg/min	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
MeOH Termination (100 wt%)	ml	20.2	21	20.3	25	16	35	35	20
Start Temperature	Deg C	55	55	55	55	55	55	55	55
Final Temperature	Deg C	57	57	55	55	55	55	55	55
Finished Batch									
Total Polymer	kg	50	50	50	60	60	85	85	60
Total Cement	kg	250	250	250	300	300	425	425	300
Solids	wt%	20	20	20	20	20	20	20	20

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Table 3: Polymer Architecture for A1-B-A2 Polymers

<u>Polymer</u>	<u>Block Size (X 10³)</u>			<u>Blockiness of Styrene in B Block (%)</u>
	<u>A1</u>	<u>B</u>	<u>A2</u>	
1	10.5	95.8	12.3	NA
2	10.5	88.1	12.2	NA
3	9.2	81.4	9.3	NA
4	9.7	82.6	10.5	1
5	13.9	126.9	17.4	5
6	10.6	90.8	11.2	4
7	10.3	89.0	12.6	7

TABLE 4: POLYMER ARCHITECTURE FOR A1-B-A2 POLYMERS

Polymer	Block Size (x1000)			Vinyl content of Butadiene (%)	Percent Styrene in B block mid (%)
	A1	B	A2		
2	10.5	88.1	12.2		
3	9.2	81.4	9.3	38	12.5
C-1*	10	80	10	35	25
C-2*	10	80	10	68	0
C-3*	10	80	10	38	0
				52.5	22.9

* actual block sizes were not measured after synthesis for these 3 polymers.

TABLE 5: TENSILE PROPERTIES

POLYMER		C-1	C-2	2	3	C-3
Stress (psi) at	50%	90.5	154.5	170.5	200	196
Stress (psi) at	100%	127.5	203	231	273.5	232
Stress (psi) at	200%	173	278	312	401.5	308
Stress (psi) at	300%	222.5	383.5	437	606.5	401
Stress (psi) at	500%	367	778.5	908	1304	775
Stress at Break (psi)	Max. Stress (psi)	3981.5	4785.5	4575.5	4723.5	4750
Stress at Break (%)	Ultimate Elongation (%)	1396.5	941.5	871.5	756	1070

CLAIMS

We claim:

1. A hydrogenated block copolymer having the general configuration A-B, A-B-A, or (A-B)_nX, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein:
 - a) prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene;
 - b) subsequent to hydrogenation about 0-10 % of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced;
 - c) each A block having an average molecular weight between about 3,000 and about 60,000 and each B block having an average molecular weight between about 30,000 and about 300,000;
 - d) each B block comprises terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units;
 - e) the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and
 - f) the weight ratio of conjugated diene to mono alkenyl arene in the B block is between about 5:1 and about 1:2.
2. The copolymer according to claim 1 wherein said mono alkenyl arene is styrene and said conjugated diene is selected from the group consisting of isoprene and butadiene.
3. The copolymer according to claim 2 wherein said conjugated diene is butadiene, and wherein about 20 to about 80 mol percent of the condensed butadiene units in block B has 1,2-configuration.

4. The copolymer according to claim 3 wherein in block B there are fewer than 20 consecutive units of any one monomer between that of each different monomer.
5. The copolymer according to claim 4 wherein each block B has a center region with a minimum ratio of butadiene units to styrene units.
6. The copolymer according to claim 3 wherein the styrene blockiness index of the block B is less than about ten percent, said styrene blockiness index being defined to be the proportion of styrene units in the block B having two styrene neighbors on the polymer chain.
7. An unhydrogenated block copolymer having the general configuration A-B, A-B-A, or (A-B)_nX, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein
- a) each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene;
 - b) each A block having an average molecular weight between about 3,000 and about 60,000 and each B block having an average molecular weight between about 30,000 and about 300,000;
 - c) each B block comprises terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units;
 - d) the total amount of mono alkenyl arene in the block copolymer is about 20 percent weight to about 80 percent weight; and
 - e) the weight ratio of conjugated diene to mono alkenyl arene in the B block is between about 5:1 and about 1:2.
8. The copolymer according to claim 7 wherein said mono alkenyl arene is styrene and said conjugated diene is selected from the group consisting of isoprene and butadiene.

9. The copolymer according to claim 8 wherein said conjugated diene is butadiene, and wherein about 20 to about 80 mol percent of the condensed butadiene units in block B has 1,2-configuration.
10. The copolymer according to claim 9 wherein in block B there are fewer than 20 consecutive units of any one monomer between that of each different monomer.
11. The copolymer according to claim 10 wherein each block B has a center region with a minimum ratio of butadiene units to styrene units.
12. The copolymer according to claim 9 wherein the styrene blockiness index of the block B is less than about ten percent, said styrene blockiness index being defined to be the proportion of styrene units in the block B having two styrene neighbors on the polymer chain.
13. A process for the preparation of a block copolymer having one or more mono alkenyl arene homopolymer blocks and one or more controlled distribution copolymer blocks of a conjugated diene and a mono alkenyl arene, comprising the steps:
- a) polymerizing a mono alkenyl arene in a first reactor in the presence of an inert hydrocarbon solvent and an organolithium initiator whereby a living homopolymer block A1 terminated with a lithium ion is formed;
 - b) adding to a second reactor an inert hydrocarbon solvent, 80 to 100% of the mono alkenyl arene monomer desired in the copolymer block B1, between 30 and 60% of the conjugated diene monomer desired in the copolymer block B1, and a randomization agent;
 - c) transferring the living homopolymer block A1 to the second reactor and starting the polymerization of the mono alkenyl arene monomer and conjugated diene monomer added in step b;
 - d) after about 20 to about 60 mol percent of the monomers of step c have been polymerized, gradually adding the remaining amount of conjugated diene monomer and mono alkenyl arene to the second reactor at a rate that maintains the concentration of the conjugated diene monomer at no less than about 0.1%

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weight until about 90% of the monomers in block B1 have been polymerized, and the percentage of the mono alkenyl arene monomer in the non-reacted monomer pool has been reduced to less than 20% weight, thereby forming a living block copolymer A1B1.

14. The process of claim 13 wherein 100% of the monoalkenyl arene monomer and about 50% of the conjugated diene monomer is added to the reactor in step b.
15. The process of claim 13 wherein said randomization agent is selected from the group consisting of cyclic ethers and aliphatic monoethers.
16. The process of claim 13 wherein said monoalkenyl arene is styrene and said conjugated diene is selected from the group consisting of isoprene and butadiene.
17. The process of claim 16 wherein said conjugated diene is butadiene.
18. The process of claim 13 including the additional step wherein additional mono alkenyl arene monomer is added to the second reactor, thereby forming a living block copolymer A1B1A2, wherein the A1 block and the A2 block each have an average molecular weight of about 3,000 to about 60,000 and the B1 block has an average molecular weight of about 30,000 to about 300,000.
19. The process of claim 13 including the additional step where the living block copolymer A1B1 is contacted with a coupling agent to form the block copolymer (A1B1)_nX where n is an integer from 2 to about 20 and X is the coupling agent residue.
20. The process of claim 18 wherein said living copolymer A1B1A2 is contacted with a terminating agent to form a terminated copolymer.
21. The process of claim 20 wherein said terminated copolymer is hydrogenated.
22. The polymer formed by the process of claim 21.
23. A process for the preparation of a linear A1B1A2 block copolymer having two monoalkenyl arene homopolymer blocks and one controlled distribution copolymer block of a conjugated diene and a mono alkenyl arene, comprising the steps:

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- a) polymerizing a mono alkenyl arene in a reactor in the presence of an inert hydrocarbon solvent and an organolithium initiator whereby a living homopolymer block A1 terminated with a lithium ion is formed;
 - b) prior to the completion of the polymerization in step a, adding to the reactor in one aliquot between 40 and 60% of the conjugated diene monomer desired in the copolymer block B1, and a randomization agent and continuing the polymerization of the mono alkenyl arene monomer and conjugated diene monomer;
 - c) after about 20 to about 60 mol % of the monomers in step b has been polymerized, gradually adding the remaining amount of conjugated diene monomer and mono alkenyl arene monomer to the reactor at a rate that maintains the concentration of the conjugated diene at no less than about 0.1% weight until about 90% of the monomers in block B1 have been polymerized, and the percentage of the mono alkenyl arene monomer in the unreacted monomer pool has been reduced to less than 20% weight, thereby forming a living copolymer block copolymer A1B1 ;
 - d) adding additional mono alkenyl arene monomer to the reactor, thereby forming a living copolymer A1B1A2, wherein the A1 block and the A2 block each has an average molecular weight of about 3,000 to about 60,000 and the B1 block has an average molecular weight of about 30,000 to about 300,000.
24. The process of claim 23 wherein said living copolymer A1B1A2 is contacted with a terminating agent to form a terminated polymer.
25. The process of claim 24 wherein said terminated polymer is hydrogenated.
26. The process of claim 15 wherein said randomization agent is an aliphatic monoether.
27. The process of claim 26 wherein said aliphatic monoether is diethyl ether.

28. A hydrogenated block copolymer having the general configuration A-B, A-B-A, or (A-B) n X, where n is an integer from 2 to about 30, and X is coupling agent residue and wherein

- a) prior to hydrogenation each A block is a mono alkenyl arene homopolymer block and each B block is a controlled distribution copolymer block of at least one conjugated diene and at least one mono alkenyl arene;
- b) subsequent to hydrogenation at least about 90 % of the arene double bonds have been reduced, and at least about 90% of the conjugated diene double bonds have been reduced;
- c) each A block having an average molecular weight between about 3,000 and about 60,000 and each B block having an average molecular weight between about 30,000 and about 300,000;
- d) each B block comprises terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units;
- e) the total amount of mono alkenyl arene in the hydrogenated block copolymer is about 20 percent weight to about 80 percent weight; and
- f) the weight ratio of conjugated diene to mono alkenyl arene in the B block is between about 5:1 and about 1:2.

29. The copolymer of claim 28 wherein said mono alkenyl arene is styrene and said conjugated diene is selected from the group consisting of isoprene and butadiene.

30. The copolymer of claim 29 wherein said conjugated diene is butadiene, and wherein about 20 to about 80 mol percent of the condensed butadiene units in block B have 1,2-configuration.

31. The copolymer of claim 30 wherein in block B there are fewer than 20 consecutive units of any one monomer between that of each different monomer.

32. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been grafted with an acid compound or its derivative.

33. The block copolymer of claim 32 wherein said acid compound or its derivative is selected from the group consisting of maleic anhydride, maleic acid, fumaric acid, and their derivatives.
34. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been grafted with a silicon or boron containing compound.
35. The block copolymer of claim 34 wherein the block copolymer of claim 1 has been grafted with a silicon compound containing at least one alkoxy group, acetoxy group, or oximido-containing group.
36. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been grafted with at least one ethylene oxide molecule.
37. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been grafted with at least one carbon dioxide molecule.
38. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been metallated with an alkali metal alkyl.
39. A functionalized selectively hydrogenated block copolymer wherein the block copolymer of claim 1 has been grafted with sulfonic functional groups.
40. The block copolymer of claim 39 wherein at least 50 percent of the sulfonic functional groups are present as zinc salts.

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ABSTRACT OF THE DISCLOSURE

The present invention is a novel block copolymer containing a controlled distribution copolymer block of a conjugated diene and a mono alkenyl arene, where the controlled distribution copolymer block has terminal regions that are rich in conjugated diene units and a center region that is rich in mono alkenyl arene units. Also disclosed is a method for manufacture of the block copolymer.

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Figure 1. Monomer distribution in Bd/S block of S-Bd/S-S Block Copolymer #3 .

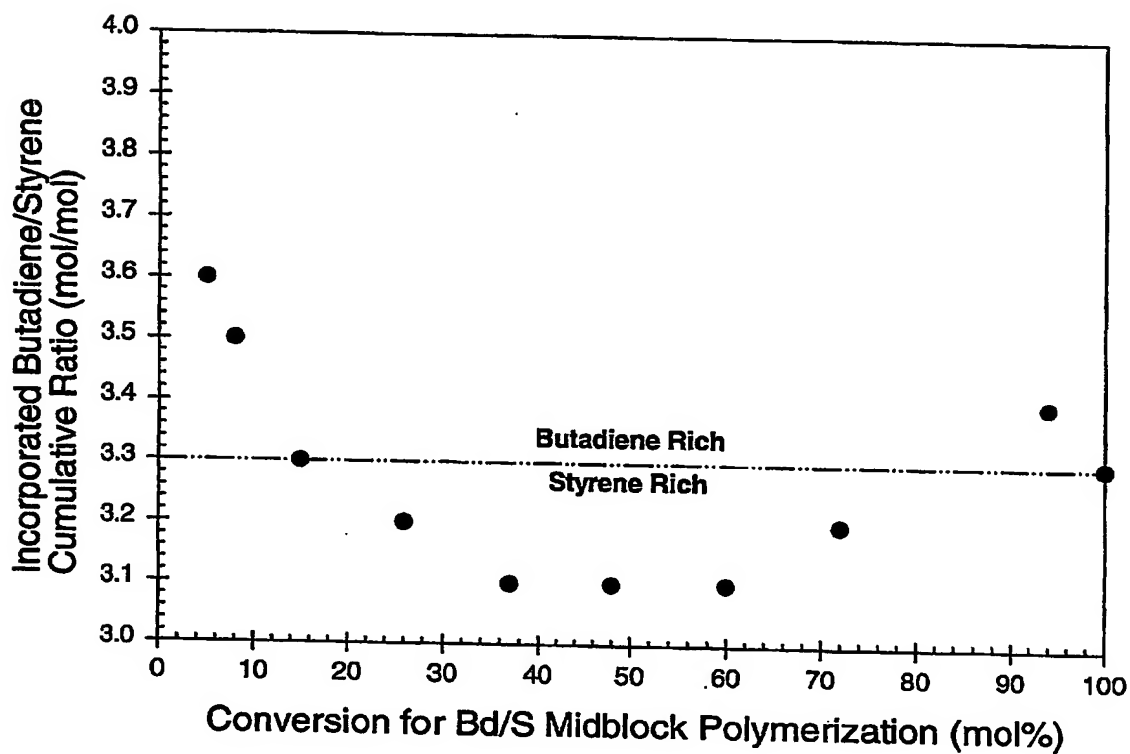


Figure 2. Monomer distribution in Bd/S block of S-Bd/S-S Block Copolymer 6.

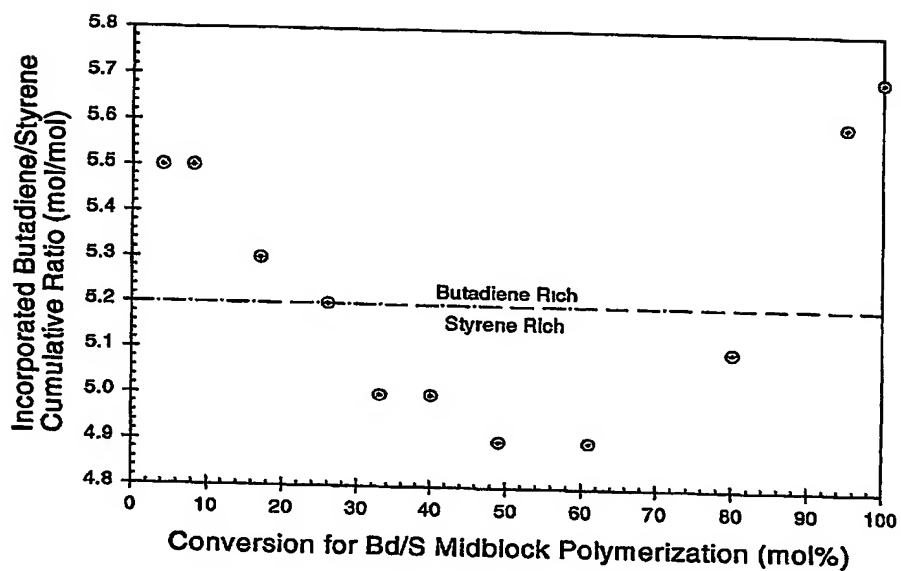
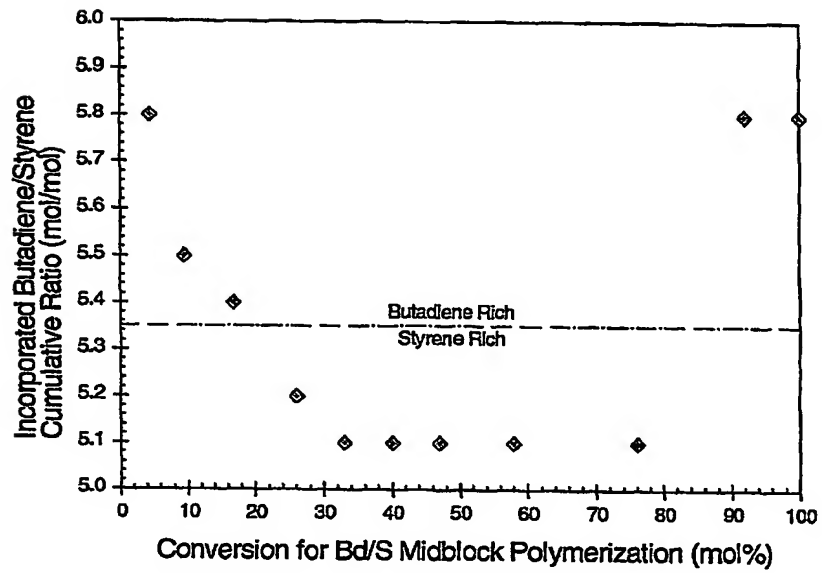


Figure 3. Monomer distribution in Bd/S block of S-Bd/S-S Block Copolymer #7.



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Figure 4

**Tensile Properties of Styrene Containing Midblocks
Compared to Normal and High Vinyl Polymers.**

